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COPOLYMERIC SULFUR – PREPARING AND USING

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ABSTRACT: This work brings original results gained by myself from preparation of copolymeric till multicomponents copolymeric sulfur as vulcanizing agents of unsaturated rubber. Forepart solving is guarded by 1 SK patent [1]. Minority important results were proclaimed and published on academic conferences [5-8]. We have acquired results utilizable on acquirement foundation for set-out of new sulfuric vulcanization agents for unsaturated rubbers from arrangements of copolymeric till multicomponets copolymeric sulfur. From science-technical, as well as economic views, or economical accessibility. It looks that comonomers with sulfur are only following ones: dicyclopentadiene, styrene, oligomers of styrene, dimmers of α-metylstyrene, dimers of pyrolysis C_5 fraction, mixture saturated and unsaturated carboxyl acids $C_{16} – C_{22}$, and their methyl- and ethylesters, as well as oil acid and stearic acid.
Optimal parameters for arrangements of copolymer till multicomponents sulfur are: temperature 128 ± 2 °C, time 240 min. and contents of comonomers is 10 till 20% of stuff. Saturated comonomers hydrocarbon chain fits to temperature 150 ± 2 °C and reaction time 120 - 240 min. Providing pattern copolymer till multicomponets copolymeric sulfur, it'll ride absolutely copolymer, on the proviso that we used identification bond C-S-C-, -C-S-S-C-, -C-S-S_n-S-C-, -C-NH-, -C-N-(R)-. At the same time we utilize FTIR and NMR.

KEY WORDS: sulfur, copolymerization, vulcanizing agents, rubber

1. INTRODUCTION

Sulfur was known in archaic times as brimstone, and mentioned as an agent of divine retribution in the Bible [2]. It reacts chemically with the raw gum elastomer forming cross-links between the polymer chains, resulting in a more dimensionally stable and less heat-sensitive product. Its cost is relatively low but its function is essential. It is available in different particle sizes (fineness) as rubbermaking sulfur, and it can also have a small quantity of oil added if we want to reduce its dust in the air during handling. Rubbermakers sulfur is a sulfur suitable for vulcanizing rubber; it has low ash content, low acidity and sufficient fineness for adequate dispersion and reaction. The finer particle sizes, coated with magnesium carbonate, assist its dispersion in elastomers such as nitrile. Sometimes, as the sulfur level in a compound is increased, some of it can slowly bloom to the surface. For example, Heinisch [3] mentions that sulfur levels, which are as low as around 1 phr (at room temperature) might bloom. Blooming occurs if an additive dissolves totally in the polymer at the processing temperature but it is only partially soluble at ambient temperature. In this situation some of the additives precipitate out of solution on cooling, collecting on the surface of the polymer mass, causing a bloom. In this case, a highly 'polymeric' (amorphous) form of sulfur, known as insoluble sulfur, is available to reduce this problem, although dispersion in the compound can be more difficult. Although bloom does not generally affect a product's performance it is aesthetically displeasing. In the uncured compound, bloom can reduce tack needed in building operations (such as plying up uncured sheets of rubber to obtain thicker sheets).

2. USED MATERIALS

Sulfur S_8 = cyclooctameric sulfur from Clausus process (producer Slovnaft Bratislava); contents of sulfur: 99.5 wt. %; contents of organic materials: 0.1 wt. %; melting point: 112 – 119 °C.
Dimers of α-methystyrene (α-MS) = unsaturated dimers of α-MS (2,4-diphenyl-4-methyl-1-penten a 2,4-diphenyl-4-methyl-2-penten) with additions of (in wt. %): kumen = 0.01; α-MS = 1.53; alkylbenzene = 1.22; acetofhenon = 9.07; dimethylphenylkarbinol = 0.24; phenol = 0.02.
Dimers of pyrolitic C_5 fraction = distilling rest of dimerization pyrolytic C_5 fraction from pyrolysis petroleum fractions (producer Slovnaft Bratislava); bromine number = 254.3 g Br_2/100 g of material;
Organic acids = mixture of organic unsaturated acids of rapsol oil (C_{16} – C_{22}); producer Polychem Prievidza; contents (in wt. %): palmit acids = 4, stearic acids = 2, oleic acids = 60, linolic acids = 20, linolenic acids = 10, eikozanic acids = 2.
Rapsol oil – pure (rafined)
Diens = oligomérs of 1,3-butadiene (Krasol LB 3000); producer Kaučuk, Kralupy nad Vltavou; viscosity (25 °C) = 10 400 mPa.s; average molecular weight = 10 059 $g.mol^{-1}$; density = 0.9520 $g.cm^{-3}$.
DCPD = dicyclopentadiene (pure); producer Výzkumný ústav anorganické chemie Ústí nad Labem; contents (wt. %): dicyclopentadiene = 93.63; trimers of cyclopentadien = 0.45; piperylene = 0.89; izoprene = 3.20.
Oleic acid - pure; producer: Lachema Brno; molecular weight = 282.47 $g.mol^{-1}$; melting point = 14 °C.

3. PREPARATION OF COPOLYMERIC SULFUR

Because of very undemanding preparation of copolymeric sulfur [6-8] and also accessibility of raw materials and very good mechanical properties of prepared vulcanizates, we have decided to prefer more detailed research of reaction conditions and we tested different ratios of cyclooctameric sulfur.

Tab. 1: Reaction components and reaction conditions of preparing copolymeric sulfur

	Contents of cyclooctameric sulpfur [wt. %]	Reaction conditions
1	Sulfur (85) + diens (3.75) + rapsol oil (11.25)	240 min, 128 ± 2 °C
2	Sulfur (85) + diens (11.25) + rapsol oil (3.75)	240 min, 128 ± 2 °C
3	Sulfur (90) + diens (2.5) + rapsol oil (7.5)	240 min, 128 ± 2 °C
4	Sulfur (90) + diens (7.5) + rapsol oil (2.5)	240 min, 128 ± 2 °C
5	Sulfur (85) + diens (11.25) + dimers of C_5 fraction (3.75)	240 min, 128 ± 2 °C
6	Sulfur (85) + diens (3.75) + dimers of C_5 fraction (11.25)	240 min, 128 ± 2 °C
7	Sulfur (85) + dimers of α-MS (3.75) + dimers of C_5 fraction (11.25)	240 min, 128 ± 2 °C
8	Sulfur (85) + dimers of α-MS (11.25) + dimers of C_5 fraction (3.75)	240 min, 128 ± 2 °C
9	Sulfur (85) + dimers of α-MS (11.25) + acids of rapsol oil (3.75)	180 min, 150 ± 2 °C
10	Sulfur (85) + dimers of α-MS (3.75) + acids of rapsol oil (11.25)	180 min, 150 ± 2 °C
11	Sulfur (85) + dimers of α-MS (3.75) + acids of rapsol oil (11.25)	180 min, 128 ± 2 °C
12	Sulfur (85) + dimers of C_5 fraction (11.25) + acids of rapsol oil (3.75)	360 min, 128 ± 2 °C
13	Sulfur (85) + dimers of C_5 fraction (11.25) + acids of rapsol oil (3.75)	480 min, 128 ± 2 °C
14	Sulfur (85) + dimers of C_5 fraction (3.75) + acids of rapsol oil (11.25)	180 min, 128 ± 2 °C
15	Sulfur (85) + dimers of C_5 fraction (3.75) + acids of rapsol oil (11.25)	240 min, 128 ± 2 °C
16	Sulfur (85) + dimers of C_5 fraction (11.25) + acids of rapsol oil (3.75)	240 min, 128 ± 2 °C
17	Sulfur (85) + DCPD (3.75) + acids of rapsol oil (11.25)	240 min, 128 ± 2 °C
18	Sulfur (85) + DCPD (11.25) + acids of rapsol oil (3.75)	240 min, 128 ± 2 °C
19	Sulfur (85) + oleic acid (11.25) + dimers of C_5 fraction (3.75)	120 min, 128 ± 2 °C
20	Sulfur (85) + oleic acid (11.25) + dimers of C_5 fraction (3.75)	240 min, 128 ± 2 °C
21	Sulfur (85) + oleic acid (3.75) + dimers of C_5 fraction (11.25)	120 min, 128 ± 2 °C
22	Sulfur (85) + oleic acid (3.75) + dimers of C_5 fraction (11.25)	240 min, 128 ± 2 °C

Copolymeric sulfur has been prepared with cyclooctameric sulfur containing organic components. Ratio components of copolymeric sulfur and reaction conditions are described in Tab. 1. Share of sulfur was 85 wt. %.

We melted the reaction mixture for a period of 5 minutes; next step was that the reaction mixture was rapidly mixed with mechanical stirrer in the inert atmosphere for the time of 180 - 480 minutes. Reaction temperature was 128 ± 2 or 150 ± 2 °C. After 15 minutes of the reaction time homogeneous mixture was formed. Final products were solid, dark and fragile. Then they were grinded to dust with particle size lower than 0.071 mm.

4. USING COPOLYMERIC SULFUR AS VULCANIZING AGENT

We studied the efficiency of copolymeric sulfur as a vulcanizing agent for tire bead mixture, which is utilized for production of bead of car radial tires. As comparable standard, we have prepared mixture with polymeric sulfur (Sulfur N), which is commonly used as vulcanizing agent. The preparation of rubber mixtures was made by two-step mixing according to Slovak standard STN 62 1425. In the second step of rubber mixture we tested samples as vulcanizing agents and other vulcanizing admixtures – accelerator of vulcanization (Vuchtalink) and inhibitor of overvulcanization (Duslin G80). The amount of sulfur in samples was calculated in order to achieve equal content of sulfur in the mixture as present in the standard (Sulfur N). The mixing of the second step was made at temperature of 110 °C of laboratory mixing machine BRABENDER. We made vulcanizing curves for all mixtures. All mixtures show very low reversion of vulcanizing curves. Individual vulcanizing characteristics were calculated from vulcanizing curves (Tab. 2).

Tab. 2: Vulcanizing and processing characteristics of rubber mixtures

	M_H [N.m]	M_L [N.m]	t_{02} [min]	$t_{c(90)}$ [N.m]	R_V [min.$^{-1}$]	Scorch time, 120 °C [min.]	Viscosity Mooney (100 °C, 1+4, ML)
Sulfur N	15.0	65.0	4.5	21.0	5.88	62.0	57.1
1	14.5	68.0	5.5	22.0	6.06	58.4	66.0
2	12.0	63.0	6.0	22.0	6.25	57.4	60.7
4	14.5	68.0	5.5	21.1	6.45	57.2	61.5
7	12.0	64.0	5.0	19.0	7.14	63.4	45.3
8	12.0	64.0	5.0	19.0	7.14	63.4	45.3
12	12.0	71.0	4.5	18.0	7.41	39.8	54.7
13	17.0	70.0	4.5	19.5	6.67	49.0	52.2
14	16.0	68.0	5.0	20.0	6.67	46.2	52.3
16	15.0	69.0	4.5	19.0	6.90	47.2	60.2
18	15.0	68.0	4.0	14.5	8.08	49.9	52.0
21	16.0	72.0	5.5	19.0	7.41	50.3	52.5
22	16.5	72.5	4.5	20.0	6.45	46.2	56.3

These vulcanizing curves are steeper in comparison to polymeric sulfur. It shows that vulcanizing time is shorter for about 3 minutes. We made vulcanizing characteristics of the rubber mixtures at 150 °C during 60 minutes of registration in vulcameter Monsanto. All vulcanizing curves of rubber mixtures have increasing torsional moment. Values of the vulcanizing parameters are comparable with parameters of rubber mixture with polymeric sulfur, which was chosen as reference material. From the comparison of the vulcanizing curves, respectively parameters, it is clear that vulcanization is faster (for about 5 %) in comparison to the mixture with polymeric sulfur, and also vulcanizing curves of mixtures are steeper than those with polymeric sulfur.

Vulcanized mixtures in the forms of plates were stored for 24 hours. Then we prepared specimen in the form of both sides shovels for tensile tests by cutting the test. Specimen was used in the form of rings for hardness test and it was used in the form of "graves" for designation of the tear strength. Cut samples were conditioned for at least 16 hours at examinational temperature and then we determined mechanical properties. Measured values of mechanical properties are shown in Table 3.

Tab. 3: Physical-mechanical properties of rubber mixtures

	Hardness [Sh A]	Elongation [%]	Strength [MPa]	Rebound resilience [%]	Modulus 300 [MPa]	Tear strength 20 °C [kN/m]	Tear strength 90 °C [kN/m]
Sulfur N	58.8	441	19.26	59.4	13.96	51.74	29.36
1	61.6	432	14.52	58.9	10.46	54.36	40.52
2	60.2	430	15.02	59.1	13.13	54.73	31.44
4	60.5	427	18.02	59.7	12.73	52.92	32.28
7	59.1	421	17.64	59.6	12.62	54.33	28.31
8	58.7	589	17.35	62.9	7.65	55.89	39.99
12	58.8	441	19.62	59.4	13.96	51.74	29.36
13	60.4	528	17.26	51.7	9.05	42.20	24.92
14	60.6	396	13.31	50.23	10.22	44.23	26.21
16	60.2	480	17.05	55.27	10,30	55.65	33.12
18	59.6	520	18.65	50.69	10.87	58.00	35.45
21	60.8	460	15.94	51.60	9.43	44.44	22.09
22	58.4	506	17.55	50.23	10.05	49.52	27.99

5. CONCLUSIONS

We can conclude from the achieved results that from the point of view of vulcanizing agent's incorporation to rubber mixtures, copolymeric sulfur with 10 - 15 wt. % of organic portion is better incorporable than polymeric sulfur. At optimum amount copolymeric sulfur applied as vulcanizing agent and regarding mechanical properties are comparable with polymeric sulfur (Sulfur N). However, it evidently performs over the standard in tear strength at 20 °C and at 90 °C respectively. Also material hardness properties are better. Moreover, copolymeric sulfur accelerates vulcanization time for about 5 %. Its utilization seems to be interesting from several points of view, as effective, safe, environment-friendly and also potentially technically and economically available vulcanizing agent for vulcanization of unsaturated rubbers.

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